Chapter 8
Effects of Reactor Wall Properties, Operating Conditions and Challenges for SCWG of Real Wet Biomass

Mohammad S.H.K. Tushar, Animesh Dutta, and Chunbao (Charles) Xu

Abstract Hydrogen is considered the cleanest fuel as it does not create any pollution during combustion. However, hydrogen is not readily available in nature as a primary energy source, but a secondary energy generated from the primary energy sources via various conversion processes. Supercritical water gasification (SCWG) process in contrast to the conventional gasification process does not require biomass drying, and rather it uses the moisture and external water in the reaction. Much research has been performed on SCWG of various types of biomass for hydrogen production, where numerous reactors made from different materials were used. Various operating conditions were also widely studied, such as catalysts, temperature, pressure, feed concentration etc. Researchers have tried quartz reactors to avoid corrosion of metallic reactors due to the supercritical water, but the overall performance was not satisfactory as the total gas yield and H_2 yield were less compared to any metallic reactor. Using catalysts improved the overall gas and hydrogen yield but the common challenge is the supported catalysts becoming deactivated over a longer operating time. Temperature has the most prominent and positive effect on H_2 yields, while pressure does not have any significant effect rather it has complex effects on the process. A higher concentration of the feed increases CO_2 production, and a lower concentration increases H_2 and CH_4 yields. Moreover, the major challenge of SCWG is feeding real biomass into the reactor. Most of researchers used model biomass or fractions of biomass (such as

---

M.S.H.K. Tushar • A. Dutta (✉)
Mechanical Engineering Program, School of Engineering, University of Guelph,
Guelph, ON N1G 2W1, Canada
e-mail: adutta@uoguelph.ca

C. Xu (✉)
Institute for Chemicals and Fuels from Alternative Resources, Department of Chemical
and Biochemical Engineering, Western University, London, ON N6A 5B9, Canada
e-mail: cxu6@uwo.ca

Z. Fang and C. Xu (eds.), *Near-critical and Supercritical Water and Their Applications for Biorefineries*, Biofuels and Biorefineries 2, DOI 10.1007/978-94-017-8923-3_8,

© Springer Science+Business Media Dordrecht 2014

cellulose or lignin) for conversion. Little literature work was reported on SCWG of real biomass in continuous flow reactors, mostly in batch reactors. Therefore, this chapter aims to discuss about the effects of the reactor wall properties, operating parameters on supercritical water gasification of real wet biomasses and the associated operating challenges.

Keywords Hydrogen • Supercritical water gasification • Real biomass • Operating parameters • Operating challenges • Batch process • Continuous process • Feeding technologies • Reactor types

8.1 Introduction

Due to ever increasing energy demand, increasing trend of fossil fuel price and need to reduce the dependency on fossil fuels, researchers are in search for renewable but environmentally benign energy sources. Biomass is one of the options that have been studied by the researchers for its various advantages, e.g., its renewability and wide availability. However, biomass has disadvantages like low bulk density, high alkali contents particularly for some agricultural feedstock, and a high moisture content. Although indigenous alkali metal contents of biomass have positive effect on hydrogen production by gasification leading to less char/coke production [1, 2], it is well known that the presence of alkali metals creates agglomerates which significantly reduces the performance of conventional fluidized bed gasifiers. A high moisture content of biomass makes conventional thermochemical processes less energy efficient, while in supercritical water gasification (SCWG) process, high moisture content is an advantage as the process employs water, at its critical point (374 °C and 22.1 MPa), as a reactive medium.

Hydrogen production plays a very important role in the creation of hydrogen economy. Hydrogen production is mainly from steam reforming methane, but producing hydrogen from renewable and inexpensive sources is certainly more environmentally friendly and promising. A large number of different processes have been studied for hydrogen production from biomass. The methods of hydrogen production from biomass can be divided to two main groups: thermochemical processes (pyrolysis, gasification and reforming) and biochemical processes (biophotolysis, gas fermentation). Biomass consists of three main chemical components: cellulose, hemicellulose, and lignin. Among these components, lignin cannot be easily converted to gaseous product via biochemical conversion, whereas it can be converted completely in thermochemical conversion [3]. Thus, thermochemical gasification processes for hydrogen production are more advantageous as they are feedstock insensitive [4].

While typical biomass such as rice husk has a low energy content of ∼15 MJ/kg (dry-and-ash-free or daf), conventional biomass gasification process requiring biomass drying, where a major portion of heat is used for drying, leads to a negative net energy production [5, 6]. Therefore, it is not economically viable to convert wet lignocellulosic biomass by traditional techniques like pyrolysis, combustion, and gasification due to high cost and energy requirements for water evaporation. Wet biomass can be converted into fuel gas rich in either hydrogen or methane by hydrothermal gasifying in hot compressed water. In a hydrothermal process at pressure higher than 20 MPa, compared to ambient condition, the heat of evaporation of water is very marginal, so high thermal efficiencies can be obtained although the feedstock has low dry matter content. In addition, ionic reactions are promoted in hot compressed water through radical routes which leads to lesser char formation [7, 8]. This provides a major impetus for the use of hot compressed water as a reaction medium for energy recovery from organic wastes. Hot compressed water at above water's critical points (374 °C and 22.1 MPa) proved to be more reactive for biomass gasification. SCWG of wet biomass produces hydrogen-rich gas products of a high efficiency and lower char and tar formation. Table 8.1 presents some detailed comparison between various thermochemical processes [9–11].

Solvolysis of hemicellulose and lignin macromolecules starts at temperatures above 190 °C when biomass is heated in liquid water [13–17]. All of the hemicellulose and much of the lignin can dissolve in hot-compressed water at 220 °C after only 2 min. The remaining lignocellulosic solids undergo solvolysis and pyrolysis at higher temperatures [18], accompanied by a phenomenal mixture of hydrothermolysis reactions such as isomerization, dehydration, fragmentation, and condensation of intermediate products, etc. Besides the hydrothermolysis reactions, steam reforming (Eq. 8.1), water-gas shift reactions (WGS) (Eq. 8.2), and methanation reactions (Eq. 8.3) also play an important role in SCWG, responsible for the generation of hydrogen-rich syngas [19–22].

Steam reforming:

$$CH_xO_y + (1-y)\,H_2O \rightarrow CO + \left(1 - y + \frac{x}{2}\right)H_2 \tag{8.1}$$

Water-gas shift:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \tag{8.2}$$

Methanation:

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O \tag{8.3}$$

Modell [23] found that wood (maple sawdust) can be completely solubilized in supercritical water, but less than 40 % of carbon in the feedstock was converted to gases due to limited gasification at temperatures below 380 °C. In addition, catalysts (including Ni, Co/Mo and Pt on alumina) did not show significant effect on the reaction chemistry under the conditions of study. Amin et al. [24] did some related experiments using glucose as a model compound for SCWG, producing 100 % conversion but with a very low gas yield. The gas produced contained less than 20 wt% of the carbon in the glucose feedstock.

Table 8.1 Comparison of various thermochemical technologies for biomass conversion [9–11]

Technology	Major biomass feedstocks	Energy or fuel produced	Advantages	Disadvantages
Direct Combustion	Wood, forestry residues, agricultural waste, and municipal solid waste	Heat Steam Electricity	1. The simplest form of biomass conversion process to obtain heat 2. Low emission of NOx and SOx, [12] 3. High efficiency in terms of heat (>90 %)	1. High investment and operating costs 2. High particulate emission 3. High CO and intermediate aromatic products generation 4. Agglomeration, sintering because of higher alkali content in some biomass such as crop residue, and corrosion in heat transfer surfaces because of a relatively higher Cl content
Conventional steam/air gasification	Wood, forestry residues, agricultural waste, and municipal solid waste	Low or medium-Btu producer gas	1. Possible for small scale power generation. 2. Relatively high conversion efficiencies 3. Modest investment costs	1. Requiring special technical and managerial skills for plant operation 2. Sensitive to the quality of fuel 3. Ash agglomeration 4. Severe tar and char formation 5. Depending on types of biomass (turndown ratio)
Supercritical water gasification (SCWG)	Wood, forestry residues, agricultural waste, municipal solid waste, sewage sludge, and model biomass	Hydrogen Methane	1. Suitable for wet biomass (moisture content > 70 %) 2. High H_2 gas yield 3. Unique properties of supercritical water (non-polarity, high diffusivity, absence of mass transfer, etc.) favoring gasification of biomass 4. Higher yield of gas products due to high reaction rates	1. High reaction pressure (>22 MPa) leading to high reactor costs 2. Continuous feeding of real biomass to a SCWG reactor being very challenging 3. SCW is highly corrosive in nature, posing challenge in materials for reactor manufacture

Pyrolysis	Wood, forestry residues, agricultural waste, and municipal solid waste	Pyrolysis oil (bio-oil), biochar	1. Relatively mature technology with large scale production demonstrated 2. Produces valuable products (bio-oil and bio-char)	1. Markets are yet to be developed for the bio-oil and bio-char products 2. Less capable to handle wet biomass, as wet biomass requires a costly drying process
Carbonization (Torrefaction)	Wood, forestry residues, agricultural waste, and municipal solid waste	Biochar	1. Improved physical characteristics of biomass 2. A higher energy content than the original biomass (per unit volume) 3. Reduced moisture content 4. Making biomass friable	1. Low enhancement in volumetric density 2. No significant improvement in energy density 3. Unable to reduce alkali content from ash
Hydrothermal liquefaction (HTL)	Wood, forestry residues, and agricultural waste	Liquid oil (biocrude), biochar, and some gases	1. Suitable for wet biomass (moisture content > 70 %) 2. Feedstock insensitive 3. Biocrude has higher heating values than pyrolysis oils 4. Yielding an energy efficiency of 85–90 % 5. Biocrude can recover more than 70 % of the feedstock carbon content	1. Not yet demonstrated in a commercial scale 2. Lower overall yield of oil (biocrude) 3. Continuous feeding of real biomass in a reactor being challenging

SCW is a green solvent and highly reactive for biomass thermochemical conversion reactions. Non-polar organic compounds can dissolve in SCW while they cannot normally dissolve in liquid water or steam. The kinetic limitations associated with mass transfer between different phases in a reactor can be effectively eliminated in SCW due to the absence of the phase boundaries and high diffusivity of gas in SCW, leading to rapid and complete reactions [25, 26]. As such, higher conversions of the solid material to fuel gas, and less solid residue can be achieved by SCWG relative to conventional direct or indirect air- or steam-blown gasification [27, 28]. Also, SCW gasification process can operate in a directly heated gasifier, or an indirectly heated reactor [29].

The objectives of this work are to discuss the effects of reactor types and operating conditions on SCWG of real wet biomass. The key operating conditions for SCWG include temperature, pressure, residence time, initial concentration, types of catalysts and feedstock. In addition, challenges of SCWG of real biomass are summarized.

8.2 SCWG with Different Types of Reactors

Various types of batch and continuous reactors have been employed for SCWG, as summarized as follows.

8.2.1 Batch Reactors

One of the many reasons for using batch reactors for SCWG over continuous processing is that it allows for the collection of significant data sets in a reasonably short period of time. In addition to this, it avoids the challenge of pumping feedstock into a SCWG process under very high pressure, and in batch reactors solid biomass can be used directly which however is extremely difficult in continuous operation [30]. As an inherent feature of batch reactors, the feedstock is heated up at a relatively low rate, when it starts to decompose during heating. Usually tar and char are generated during heating due to hydrothermal pyrolysis prior to gasification reactions, although they can further gasify to form gaseous product. However, amount of tar and char production strongly depends on the heating rate and the type and substrate concentration of the feedstock in SCWG. As such, it is of a great interest understand the performance of batch reactors for SCWG of various feedstocks.

Experiments for liquefying cellulose in hot-compressed water in a batch reactor produced 70 % conversion of biomass at a residence time under 60 min and temperatures ranging from 200 to 400 °C under pressures ranging from 8 to 22 MPa using nickel catalysts and alkali salts [31, 32]. The use of a catalyst significantly reduced residual chars and tars. Another important study of gasification of organic wastes in hot compressed water (350 °C and 20 MPa, 2 h) resulted in over 85 % biomass conversion [33]. A high methane yield was observed from the gasification of aliphatic hydrocarbon in SCW at lower temperatures, while much less time is required to obtain similar biomass conversion with a continuous reactor [34].

Batch reactor systems build using different materials have been studied by researchers. Most of the systems were purchased commercially rather than constructed in-house. Most commonly, autoclave batch reactors were used in various studies [27, 28, 35–41]. Besides these autoclave reactors, uses of various other types of batch reactors, e.g., conventional batch reactors [30, 42–46], tumbling batch reactor [47], small unstirred batch reactor [48], micro volume batch reactor [49], mini batch reactor [50] and in-house made reaction vessel [51] were reported. Most of these batch reactors are made of stainless steel, mainly 316 L [27, 30, 35, 36, 38–40, 44, 46, 50], some are made of Inconel 625 [28, 41, 47, 51] and a few are made of quartz [43, 49]. Catalytic effects of reactor wall on SCWG efficiency in batch reactors are discussed in a separate section (Sect. 8.8) of this chapter. It shall however be noted that the batch reactor wall could be passivated by carbon deposition after a few runs of experiments in the batch reactor [42, 52].

8.2.2 Continuous Flow Reactors

Continuous flow reactors (predominantly tubular reactors) proved to be more efficient and scalable than batch reactors for SCWG of biomass. Almost all continuous flow SCWG setups are currently on a bench scale. A typical setup includes a tubular reactor [42, 48–51, 53–66] heated inside an electric furnace, and a high-pressure pump (e.g., HPLC pump) for feeding liquid biomass or model compounds. Some researchers also tested fluidized bed reactors for SCWG [36, 67] as well as continuous-stirred tank reactor (CSTR) [52, 68]. Continuous SCWG systems allow for high feed throughput which is a must for any potential scale-up of the SCWG process. Moreover, compared to batch operation the heating rate in a continuous reactor can be much faster. The benefit of employing fast heating rate is to eliminate undesired byproducts (tar and char) from the feedstock, which can cause clogging of the reactor system – the major challenge of SCWG in continuous flow tubular reactors [52, 69].

8.3 Effects of Temperature on SCWG

Temperature has dominating effects on hydrogen yield. With an increase in temperature the hydrogen and carbon dioxide yields increase while the methane yield decreases. Thermodynamically at lower reaction temperatures, H_2 and CO_2 readily react to form methane and water via the methanation reaction. A higher temperature could limit the methanation reaction and promote water gas shift reaction, leading

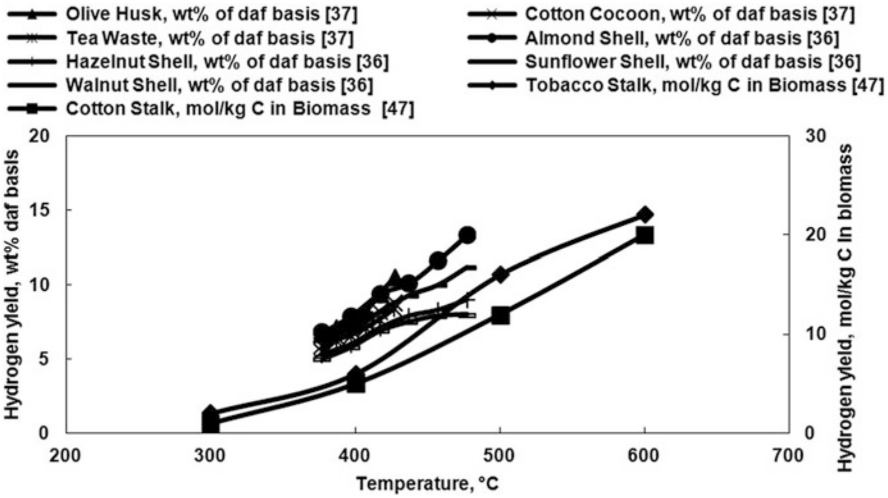

Fig. 8.1 Effects of temperature on hydrogen yield

to low CH_4 and CO formation. In a SCWG process, the presence of excess water leads to a preference for the formation of H_2 and CO_2 instead of CO. Supercritical water reforming also reduces the formation of various intermediate and complex tarry compounds such as organic acids, phenols, ketones, cresols, furfurals and aldehydes which may otherwise form in appreciable concentrations in conventional gasification processes [27, 30, 36, 38, 40, 43, 46, 49–51]. Figure 8.1 shows the effects of temperature on hydrogen yield, with data extracted from literatures cited in the legend. As clearly shown in this Figure, hydrogen yield increases with increasing temperature.

In SCWG, formation of hydrogen or methane are competing each other. Antal [70] suggested the following equations for the generation of hydrogen and methane by using glucose as a model compound to simplify the stoichiometry:

Hydrogen formation:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \Delta \mathrm{H}^o 298 = 158 KJ/mol \tag{8.4}$$

Methane formation:

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \Delta \mathrm{H}^o 298 = -134.1 KJ/mol \tag{8.5}$$

The formation reactions of hydrogen and methane have opposite characteristics. The formation of hydrogen is endothermic whereas the formation of methane is exothermic [42], which implies that with the increase in temperature, hydrogen and carbon dioxide yields increase as per the Le Chatelier's principle. On the contrary, methane yield decreases with increasing temperature based on the same principle. Temperature could also affect the formation of char and tar – byproducts

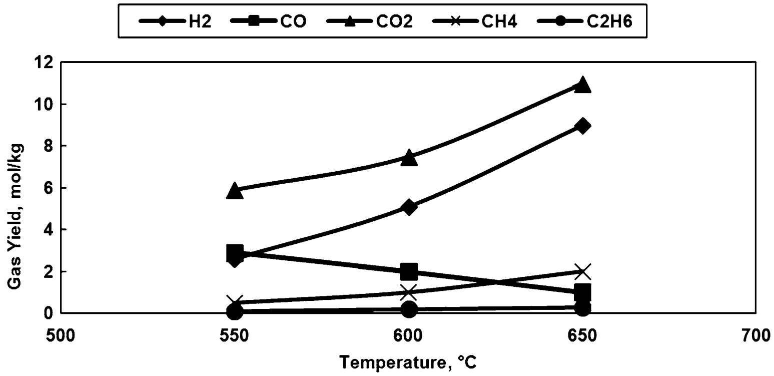

Fig. 8.2 Effects of temperature on gas yield from SCWG of corn cob. Pressure: 25 MPa; feedstock: 5 wt% corn cob + 2 wt% carboxymethyl cellulose (CMC); flow rate of feedstock: 25.05 g/min; flow rate of pre-heated water: 126.7 g/min. [69] (Reprinted with permission from International Association of Hydrogen Energy, Copyright © 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd.)

of gasification reactions. It was reported by Kruse et al. [71] that char formation could be eliminated by increasing the heating rate. Usually below the critical point, furfurals are formed upon heating of biomass (particularly glucose). However, when the temperature reaches the supercritical range furfurals would form char by condensation/polymerization with other products such as phenolic compounds derived from lignin [72]. Similarly, tar could be promoted at slower heating rates. It has been reported that temperature has a strong impact to reduction of tar formation. For instance, most of the tars would convert into gaseous product at a temperature above 700 °C [73].

Lu et al. [69] studies SCWG of corn cob at 25 MPa and the gas yield vs. temperature is shown in Fig. 8.2. It shows that H_2 and CO_2 yields increase sharply while CO decreases with the increase in temperature. Gasification efficiency (or carbon efficiency) also increases with the increase in temperature as well as residence time [65, 66, 69]. A higher temperature favors free-radical reactions, and hence enhances reaction rates, which improves gas yield [69].

8.4 Effects of Pressure on SCWG

Pressure shows complex effects on biomass gasification in SCW. With the increase in pressure, the properties of water, such as density, static dielectric constant and ion product also increase. This in turn increases the rates of the ion reactions and restrains free-radical reactions [1]. Also hydrolysis reaction plays a significant role in biomass gasification in SCW, which is promoted by the presence of H^+ or OH^-. As increasing pressure favors the ion product generation, the hydrolysis rate could

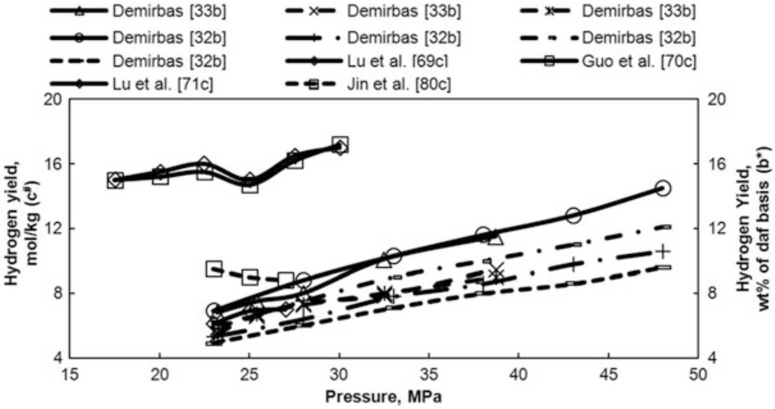

Fig. 8.3 Effect of pressure on hydrogen yield (#c = continuous reactor system, *b = batch reactor system)

be promoted. Moreover, high pressure favors water–gas shift reaction, but reduces decomposition reaction rate as per the Le Chatelier's principle. From some research work at lower temperatures [27, 38, 49], increasing pressure slightly increased the hydrogen yield, but pressure has complex effects on gas yield at higher temperatures as discussed below.

The effects of pressure on the mechanism of supercritical gasification of biomass are however very complicated. With the increase in pressure while the other parameters such as temperature, substrate concentration, and flow rate are remained constant, the density and ion product of water increase. An increase in the rates at higher pressure accelerates ion reactions that favor gas production via the hydrolysis reaction and water gas shift reaction. On the other hand, higher pressure restrains free-radical reactions, which in turn inhibits gas formation reactions via free radicals [74]. From Le Chatelier's principle, a reaction that produces more molecules is inhibited at high pressure region. Thus, the gasification process is generally favored at lower pressure [75]. The combined effects of pressure result in the complicated effects of pressure on SCWG [42]. Figure 8.3 shows that the reactor pressure does not have significant effect on SCWG of biomass in either batch or continuous reactors. The special physical and chemical properties of SCW disappear when the pressure is below the critical point, which could inhibit hydrogen production. However, operation at high pressure greatly increased operating cost. As a result, 25 MPa was very commonly used as the operating pressure for a SCWG process to balance the effects of pressure on hydrogen yield and the operating costs [76].

In summary, Temperature has predominant effect on SCWG of biomass if compared to pressure. The variation in polarity (i.e. dielectric constant) of SCW could account for the complex effects of pressure in both batch and continuous processes of SCWG. For instance, when the pressure was increased from 27.5 to 42.5 MPa at 500 °C, the dielectric constant of water increased from 1.59 to 2.6 [77]. Nevertheless, with the increase in temperature, the dielectric constant of

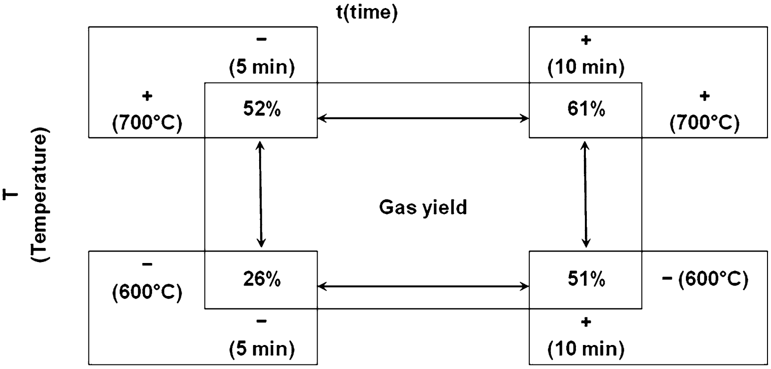

Fig. 8.4 Two-way Table illustrating the interaction of reaction temperature and time (Reprinted with permission from [30]. Copyright © 2011, Elsevier)

water decreases considerably. For example, the dielectric constant of water reduced from 4.84 to 1.59 when the temperature was increased from 400 to 500 °C at 27.5 MPa [78].

8.5 Effects of Residence Time on SCWG

From the thermodynamics perspective, complete gasification of biomass can be achieved in SCW to produce H_2 and CO_2 as the only gaseous products for a sufficiently long residence time. However, the SCWG process is usually controlled by kinetics and may take up to several hours to complete. Figure 8.4 shows the two-way interaction Table between residence time and reaction temperature, where it is clearly shown that a longer residence time favors gaseous production and hence increases the hydrogen yield with less amount of tars [30, 36, 42, 49–51].

Generally, reaction kinetics controls the gasification reactions. In continuous reactors, Sato et al. [75] found that methane and carbon dioxide production increased accompanied by decrease in tar with increasing in reaction time until 180 min but hydrogen production remained almost constant. Miller et al. [79] reported positive and significant effects of residence time on gas yield: the gasification rate increased by increasing either temperature or residence time.

8.6 Effects of Feed Concentration on SCWG

Feed concentration directly affects the gas yield. Very commonly a lower biomass concentration led to a higher gas yield (rich in H_2) [30, 36, 42, 49, 50]. Usually water is present in excess during SCWG of any biomass as water acts as both solvent and reactant in the process. At a lower biomass to water ratio, solvation during heat-up can proceed more efficiently. This in turns reduces the possibility of formation of polymerized carbonaceous material – precursors for char/tar. Guan et al. [50] found that the yield of H_2 was very sensitive to feed concentration although the total yield of carbon-containing gases was largely insensitive to this variable. For instance, hydrogen yield in SCWG of algae reduced by more than twofold as the algae loading increased from 1 to 15 wt%. Guo et al. [36] also obtained the same findings and recommended a higher reaction temperature to complete SCWG of higher concentration feedstock, which is consistent with the thermodynamic calculation.

In the case of continuous SCWG processes, feed concentration has significant effect on gasification efficiencies and yields too, although it does not show a significant effect on the gasification rate. Increased feed concentration resulted in decreased gasification and carbon efficiencies and H_2 yield but an increased CH_4 yield [36, 43, 66, 69]. From kinetics, a higher concentration leads to a higher gasification rate, which thus seems to contradict that observed in the SCWG experiments at high substrate concentration (the efficiencies and gas yield decreased). A plausible explanation is that polymerization reactions are promoted at higher feed concentration due to the formation of defiant species from the feed materials, which reduces the number of available feed molecules for gasification. Usually CH_4 yield increases at higher feed concentrations, which is likely due to the lack of water that restricts the methane reforming reaction [48–54, 62, 66].

8.7 Effects of Catalyst on SCWG

A lot of catalysts have been used for conventional thermal gasification of biomass [80]. Nonetheless, there are differences between the catalysts used for conventional thermal gasification and SCWG as the operating conditions of these two processes are different, e.g. pressure and temperature. Four types of catalysts were commonly used by the researchers which include activated carbon, metal, metal-oxide and alkali [81, 82]. Elliot [81], Calzavara et al. [82] and Guo et al. [83] reported in their reviews that to improve hydrogen formation and reduce char or tar produced inside the reactor, catalysts proved to be very effective. Alkali compounds [30, 35, 42] such as K_2CO_3, KOH, Trona ($NaHCO_3.Na_2CO_3.2H_2O$) were used in batch reactors to facilitate H_2 and CO_2 formation while reducing CO by catalyzing water–gas shift reaction. These catalysts become base when dissolved in water and affect the water–gas shift reaction to improve the gas quality, i.e., H_2 yield. Lu et al. [42] studied SCWG of some biomass in the presence of various metal/metal-oxide catalysts, including CeO_2, $nCeO_2$, $n(CeZr)_xO_2$, Pd/C and Ru/C, among which Ru/C catalyst demonstrated to be the most effective for hydrogen production.

Nickel is a metal catalyst that is usually employed not only in the conventional gasification [80], but also for SCWG. Kersten et al. [43] and Azadi et al. [45] tested several different forms of nickel catalysts in a batch reactor and obtained superior hydrogen selectivity. It is well known fact that Ni catalysts promote water–gas shift reaction. Some noble metal catalysts were also experimented for biomass SCWG.

Yamamura et al. [51] found that with RuO_2 catalyst, cellulose and glucose were almost completely gasified at 450 °C and 47.1 MPa in a reaction vessel (batch reactor). Similarly, Kersten et al. [43] observed that 1 wt% glucose solution could completely gasify with 3 wt% Ru/TiO_2 at 800 °C and 30 MPa in a quartz batch reactor. Nevertheless, nickel is much less expensive compared to the noble metal and hence nickel shows more promise for large-scale hydrogen production from biomass SCWG.

In continuous SCWG processes, similar effects as those of batch processes were observed. In a continuous SCWG process, the catalyst (both the support and the active metal) must be stable enough in supercritical water environment, not to mention it should have reasonable activity and selectivity to the target gas products (H_2, CH_4 and CO). Although numerous studies have been reported but only a few are dealing with SCWG of real biomasses in continuous reactors. In a flow reactor, addition of K_2CO_3 increases the gasification efficiency but decreases CO yield [84]. Jarana et al. [67] reported that hydrogen production was at maximum in SCWG using KOH catalyst. They concluded that the rate of the water-gas shift reaction increases by alkali salts (most probably as an acid–base catalyst). Pei et al. [62] tested a variety of catalysts: Raney-Ni, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, NaOH, KOH, LiOH, $ZnCl_2$, dolomite ($CaMg(CO_3)_2$) and olivine ($(Mg.Fe)_2SiO_4$). In presence of Raney-Ni catalyst, complete gasification was obtained with the maximum hydrogen yield up to 28.03 g/kg biomass at 400 °C and 24 MPa [62]. Chen et al. [63] used NaOH as a catalyst for gasification of wheat stalk, and found that hydrogen yield was increased. Byrd et al. [64] investigated hydrogen production in catalytic gasification of switchgrass biocrude in supercritical water employing nickel, cobalt, and ruthenium catalysts supported on titania, zirconia, and magnesium aluminum spinel supports. Their findings can be summarized as follows:

1. $MgAl_2O_4$ was not a suitable catalyst support for biocrude reforming as catalysts supported on $MgAl_2O_4$ were charred immediately;
2. Higher conversion of biocrude was achieved with ZrO_2-supported catalysts than TiO_2-supported ones. However, TiO_2 supports produced the smallest amount of char;
3. Ni/ZrO_2 produced the highest hydrogen yield whereas Ru/ZrO_2 yielded the lowest hydrogen;
4. When using Ru/ZrO_2 in SCWG, a great amount of char was formed accounting for its lowest gasification efficiency.

Rönnlund et al. [65] studied effects of KOH, K_2CO_3, NaOH and black liquor on SCWG of paper mill sludge. Similar catalytic effects were observed when adding black liquor to the sludge. This finding paved the way of improving gasification yield without expensive catalysts.

Figure 8.5 shows different reaction conditions depending on the desired gas product (H_2 or CH_4) in biomass SCWG. Minowa et al. [32] demonstrated that methane was the main product when the process temperature was between 374 and 500 °C at above the critical pressure, whereas hydrogen was the main product when the process temperature was over 500 °C under pressure above the critical pressure.

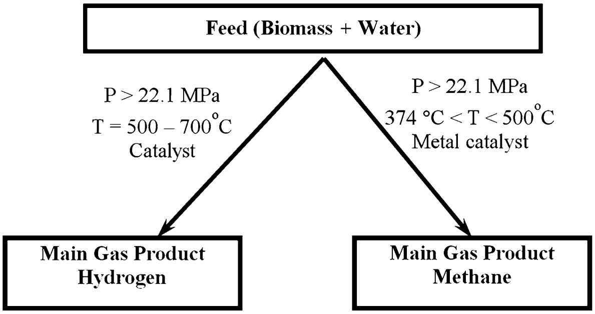

Fig. 8.5 Reaction conditions for different main products of SCWG

It is a well-known fact that alkali salts could aid in splitting of C–C bonds, which in turns assist to produce more H_2 during the SCWG. For instance, the presence of K_2CO_3 can catalyze WGS reaction in the following mechanism, leading to a higher yield of H_2 and CO_2 [85].

$$K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH \tag{8.6}$$

$$KOH + CO \rightarrow HCOOK \tag{8.7}$$

$$HCOOK + H_2O \rightarrow KHCO_3 + H_2 \tag{8.8}$$

$$2KHCO_3 \rightarrow CO_2 + K_2CO_3 + H_2O \tag{8.9}$$

8.8 Effects of Reactor Wall Properties on SCWG

Most of the reactors used for batch and continuous flow SCWG processes were made of metal alloys: such as stainless steel 316L [27, 30, 35, 36, 38–40, 42, 44–46, 50] and Inconel 625 [41, 42, 47, 51]. Only a few were made of quartz reactor [43, 49, 86]. SS 316L is an alloy of iron, chromium (16.00–18.00 wt%), nickel (10.00–14.00 wt%) and molybdenum (2.00–3.00 wt%) [87]. As most of the supercritical water reactor materials are alloy, the inner wall of the reactor might catalyze the SCWG reactions. It is well known that water becomes corrosive at its supercritical state. As a result, any nickel present in the reaction process, either as a catalyst loaded or part of reactor material will affect the reaction process. Kersten et al. [43] showed that metal reactors had higher carbon conversion and water-gas shift activity due to the catalytic effects of the metallic reactor wall, compared with quartz reactors. Resende and Savage [88] reported that the total gas yield and the H_2 mole fraction from SCWG of biomass were lower in a quartz reactor than in a stainless steel reactor at moderate water densities (~0.07 g/cm^3), which proved the catalytic

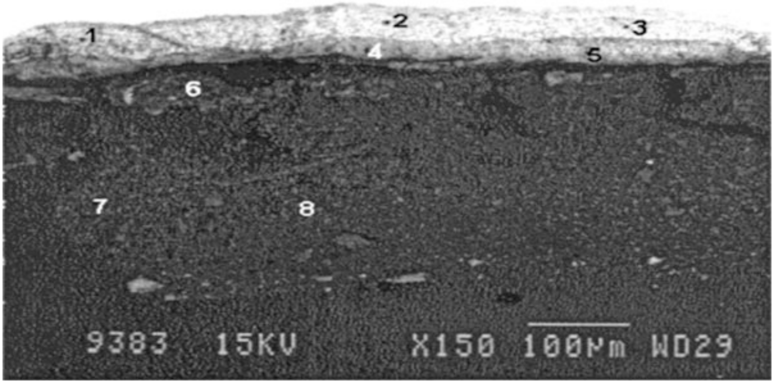

Fig. 8.6 Backscattered electron image of corrosion product on inner diameter of used Hastelloy reactor, at 150× magnification, showing analysis points 1–8. The unaltered tube metal is the brightest layer at the top of the image (Reprinted with permission from [55]. Copyright © 2000, American Chemical Society)

effects of the reactor wall on both the formation rate and composition of the gas products. However, the influence of reactor metal surfaces was found to be relatively less significant in the process that is more affected by other reaction conditions, in particular reaction temperature.

Boukis et al. [89] studied methanol reforming in supercritical water in a flow-reactor made of Inconel 625. They found chromium (Cr) and molybdenum (Mo) dissolved in the effluent and the concentration of Cr and Mo in the effluent increased with increasing reaction temperature. With further experimentation, only Ni was left on the inner wall. Antal et al. [55] studied SCWG with a reactor made of Hastelloy C-276 which is composed of mainly Ni and Fe, as well as Mo, Cr and traces of Co (cobalt), W (tungsten) and Mn (manganese). They observed that the experiments after the second run produced less amount of hydrogen but more methane. It was found out that the deposition of carbon on the reactor inner wall made the difference in the products because it reduced the catalytic effect of the reactor wall. The catalytic effect was restored by using hydrogen peroxide (H_2O_2) washing after each reaction. They analyzed ash from the reactor residues after gasification, and realized that ash from the reactor residues contains almost all types of the elements of the Hastelloy reactor, which suggests that metals of the Hastelloy alloy reactor were leached out during the SCWG. SEM analysis of the Hastelloy reactor tubing after gasification process showed heavily corroded surface. Figure 8.6 shows backscattered electron microscope image displaying two distinct layers. The darkest and porous part represents the outer most part of the inner wall which was the nearest to the reactants, and was rich in feedstock ash. The farthest part can be attributed to the solid residues from the reactants, and the brightest part at the inner side of the inner wall is the un-reacted base metal of Hastelloy. Due to the corrosion at the innermost wall, all metals except iron contained in the Hastelloy alloy reactor wall could undergo depletion by leaching after a long time-on-stream.

8.9 SCWG Operating Challenges and Possible Solutions

8.9.1 Batch Reactors

There is a concern about the high operating temperature and pressure in SCWG. The major drawback of a batch reactor is poor upscalability. Batch reactors are less economical for commercial/industrial production of bulk products. Another problem with batch reactors for SCWG of biomass is associated with reactor cleaning due to the polymerization of the decomposed products particularly at higher substrate concentrations [90]. Capillary quartz tubes as high-pressure batch reactors used for SCWG reactions are cheap and safe, but such reactor is only suitable for bench-scale testing due to its extremely small size. Moreover, the small diameter of a capillary quartz tube reactor led to non-uniform distribution of the catalyst inside the reactor thus affecting the product yield [91]. Another major disadvantage of batch reactors compared with continuous reactors is their inherent slower heating rate that could reduce the gasification efficiency due to enhanced polymerization or charring reactions at a low heating rate [30].

8.9.2 Continuous Reactors

SCWG in continuous flow reactors is a promising biomass to energy processing technology. However, due to its high operating temperature and pressure, no commercial-scale process has been built and operated so far. However, a pilot plant called “VERENA” was built in Germany. The pilot plant VERENA (a German acronym for “experimental facility for the energetic exploitation of agricultural matter”) is in operation since 2003 with a total throughput of 100 kg/h and can handle biomass-water slurry containing a maximum of 20 wt% dry biomass. The maximum designed operating pressure is up to 35 MPa and a maximum designed temperature is 700 °C. Usually the common operating conditions for the “VERENA” plant are: 50 or 100 kg/h feeding rate, up to 660 °C and 28 MPa [92, 93].

Some key challenges for SCWG processes are summarized as follows:

(a) In a supercritical water reactor, a biomass feed would take a relatively long time for being heated up. The lower heating rate would promote formation of furfurals and other unsaturated intermediate complex products, which tend to polymerize at higher temperatures to generate char, tar, and coke. This degrades the product gas quality and reduces the overall efficiency of the process [71, 94].

(b) Matsumura et al. [95] suggested for the economics of the SCWG process, it is very important to have heat exchange between the reactor effluent and the reactor feed by considering the heat balance. However, heat recovery from the high-pressure corrosive effluent and use it for the preheating of the feed material is another design problem as it would pose challenges for heat exchangers design with respect to materials selection and pressure rating for the heat exchangers.

(c) Continuous processes are commonly facing severe reactor plugging problem [55, 60]. This plugging causes an acute problem that would require forcefully shutting down the whole system [95]. Reactor plugging was mainly caused by the formation of char and tars in a flow reactor. Due to remarkably low solubility of the polar inorganic salts present in the SCWG reactors, either from the feedstock or from the reactor, they precipitate inside the reactor, forming agglomerates and coating on the inner reactor wall, which hinder heat transfer through the reactor wall. If the deposition/coating is overlooked and allowed to grow inside, there is a possibility of plugging of the reactor. These in turn lead to tedious and hectic cleaning process, and hence reduce the overall efficiency of the SCWG process [1, 96, 97].

(d) Feeding real biomass into a SCWG reactor is very important for a continuous process and has been a long-standing technological challenge for the development of SCWG technology. Dry biomasses are hard to dissolve into water to prepare gelatinous solution for the feeding purpose. A biomass pretreatment method using hot compressed water treatment (at 150 °C for 30 min), so-called ‘softening’ was successfully applied by Matsumura et al. [88] for feeding cabbage to a SCWG reactor. Antal et al. [55] used corn starch gel to mix sawdust and successfully delivered the mixture into a SCWG reactor by using a ‘cement pump’. Hao et al. [68] successfully fed solid biomass feedstock continuously into a SCWG reactor using sodium carboxymethylcellulose (CMC) as surfactant in mixing the solid biomass feedstock and water. D’Jesus et al. [60] used xanthan successfully to feed biomass continuously in to a SCWG reactor.

8.10 Conclusions

The following conclusions can be drawn from this literature analysis, focused on effects of reactor types, operating conditions and challenges for SCWG of real wet biomass:

1. The process parameters need to optimize in order to achieve better process efficiency and economics for various types of feed and concentration.
2. There is a need to develop inexpensive, long lasting, more active, more selective and durable catalysts for the gasification process.
3. Reactor plugging is one of the major operating issues that needs sufficient amount of attention. This issue can be addressed by using proper feeding mechanism and employing some novel biomass pre-treatment methods.
4. There is very limited literature work available on kinetics studies of a SCWG process [82, 83, 98–100]. The development of kinetic model requires a good formulation of the elementary steps from the feed materials to the products.

However, a more elaborate scheme of reactions describing the steps is necessary to explain the complex reactions that occur during the gasification process. Hence, a significant amount of research in this regard is urgently needed.

5. Reactor corrosion is another major issue of SCWG processes.

Acknowledgements The authors are grateful for the financial support from NSERC/FPInnovations Industrial Research Chair Program in Forest Biorefinery and the Ontario Research Fund-Research Excellence (ORF-RE) from Ministry of Economic Development and Innovation. Support from the industrial partners including FPInnovations, Arclin Canada, BioIndustrial Innovation Centre is also acknowledged. The authors (C. Xu and A. Dutta) also acknowledge the funding from NSERC via the Discovery Grant Program.

References

1. Guo L, Cao C, Lu Y. Supercritical water gasification of biomass and organic wastes. In: Momba MNB, editors. Biomass. ISBN: 978-953-307-113-8, InTech; 2010. Available from: http://www.intechopen.com/books/biomass/supercritical-water-gasification-of-biomass-and-organic-wastes
2. Kannan MP, Richards GN. Gasification of biomass chars in carbon dioxide: dependence of gasification rate on the indigenous metal content. Fuel. 1990;69(6):747–53.
3. Hemmes K, de Groot A, den Uil H. BIO-H_2. Application potential of biomass related hydrogen production technologies to the Dutch energy infrastructure of 2020–2050. ECN-C-03-028, April 2003.
4. Ni M, Leung DYC, Leung MKH, Sumathy K. An overview of hydrogen production from biomass. Fuel Process Technol. 2006;87(5):461–72.
5. Buhler W, Dinjus E, Ederer HJ, Kruse A, Mas C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. J Supercrit Fluid. 2002;22(1):37–53.
6. Penninger JML, Kersten RJA, Baur HCL. Reactions of diphenylether in supercritical water-mechanism and kinetics. J Supercrit Fluid. 1999;16:119–32.
7. Leible L, Kälber S, Kappler G, Lange S, Nieke E, Wintzer D Fürniss B. Competitiveness and CO_2 mitigation costs of biogenic residues and waste for heat and power production. In: Bridgwater AV, Boocock DGB, editors. Science in thermal and chemical biomass conversion. UK: CPL press; vol. 2. 2006. p. 1730.
8. ECN. Energy Research Centre of the Netherlands, General information, PHYLLIS, the composition of biomass and waste. 2007. http://www.ecn.nl/phyllis/DataTable.asp
9. Demirbaş A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energ Convers Manage. 2001;42(11):1357–78.
10. McKendry P. Energy production from biomass (part 2): conversion technologies. Bioresour Technol. 2002;83(1):47–54.
11. Faaij A. Modern biomass conversion technologies. Mitig Adapt Strat Glob. 2006;11(2): 335–67.
12. Jenkins BM, Baxter LL, Miles Jr TR, Miles TR. Combustion properties of biomass. Fuel Process Technol. 1998;54(1):17–46.
13. Bobleter O, Binder H. Dynamic hydrothermal degradation of wood. Holzforschung. 1980;34:48–51.
14. Bouchard J, Nguyen TS, Chornet E, Overend RP. Analytical methodology for biomass pretreatment. Part 1: solid residues. Biomass. 1990;23(4):243–61.
15. Bouchard J, Nguyen TS, Chornet E, Overend RP. Analytical methodology for biomass pretreatment. Part 2: characterization of the filtrates and cumulative distribution as a function of treatment severity. Bioresour Technol. 1991;36(2):121–31.

16. Mok WSL, Antal Jr MJ. Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water. Ind Eng Chem Res. 1992;31(4):1157–61.
17. Allen S, Kam LC, Zemann AJ, Antal MJ. Fractionation of sugar cane with hot, compressed, liquid water. Ind Eng Chem Res. 1996;35(8):2709–15.
18. Bobleter O, Concin R. Degradation of poplar lignin by hydrothermal treatment. Cell Chem Technol. 1979;13:583–93.
19. Antal MJ, Mok WS, Richards GN. Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose. Carbohydr Res. 1990;199:91–109.
20. Antal MJ, Mok WS, Richards GN. Four-carbon model compounds for the reactions of sugars in water at high temperature. Carbohydr Res. 1990;199:111–5.
21. Antal MJ, Leesomboon T, Mok WS, Richards GN. Mechanism of formation of 2-furaldehyde from D-xylose. Carbohydr Res. 1991;217:71–85.
22. Holgate HR, Meyer JC, Tester WJ. Glucose hydrolysis and oxidation in supercritical water. AIChE J. 1995;41(3):637–48.
23. Modell M. Gasification and liquefaction of forest products in supercritical water. In: Overand RP, Milne TA, Mudge LK, editors. Fundamentals of thermochemical biomass conversion. London: Elsevier Applied Science Publishers, Ltd.; 1985. p. 95–119.
24. Amin S, Reid RC, Modell M. Reforming and decomposition of glucose in an aqueous phase. In: Intersociety conference on environmental systems, San Francisco, CA, 21–24 July; 1975. ASME 75-ENAs-21.
25. Dinjus E, Kruse A. Hot compressed water – a suitable and sustainable solvent and reaction medium? J Phys Condens Matter. 2004;16(14):161–9.
26. Bazargan M, Fraser D, Chatoorgan V. Effect of buoyancy on heat transfer in supercritical water flow in a horizontal round tube. J Heat Transf. 2005;127(8):897–902.
27. Demirbas A. Hydrogen production from biomass via supercritical extraction. Energ Source. 2005;27(15):1409–17.
28. Yanik J, Ebale S, Kruse A, Saglam M, Yüksel M. Biomass gasification in supercritical water: part 1. Effect of the nature of biomass. Fuel. 2007;86(15):2410–5.
29. Hrabovsky M, Konrad M, Kopecky V, Hlina M, Kavka T. Gasification of biomass in water/gas-stabilized plasma for syngas production. Czech J Phys. 2006;56(2):B1199–206.
30. Venkitasamy C, Hendry D, Wilkinson N, Fernando L, Jacoby W. Investigation of thermochemical conversion of biomass in supercritical water using a batch reactor. Fuel. 2011;90(8):2662–70.
31. Minowa T, Ogi T, Dote Y, Yokoyama S. Methane production from cellulose by catalytic gasification. Renew Energy. 1994;5(5):813–5.
32. Minowa T, Fang Z, Ogi T. Cellulose decomposition in hot – compressed water with alkali or nickel catalyst. J Supercrit Fluid. 1998;13:253–9.
33. Elliott D, Sealock L, Baker E. Chemical processing in high pressure aqueous environment. 3. Batch reactor process development experiments for organic destruction. Ind Eng Chem Res. 1994;33(3):558–65.
34. Elliott D, Phelps M, Sealock L, Baker E. Chemical processing in high – pressure aqueous environment 4. Continuous – flow reactor process development experiments for organics destruction. Ind Eng Chem Res. 1994;33(3):566–74.
35. Schmieder H, Abeln J, Boukis N, Dinjus E, Kruse A, Kluth M, Petrich G, Sadri E, Schacht M. Hydrothermal gasification of biomass and organic wastes. J Supercrit Fluid. 2000;17(2):145–53.
36. Guo LJ, Lu YJ, Zhang XM, Ji CM, Guan Y, Pei AX. Hydrogen production by biomass gasification in supercritical water: a systematic experimental and analytical study. Catal Today. 2007;129(3):275–86.
37. Yanagida T, Minowa T, Nakamura A, Matsumura Y, Noda Y. Behavior of inorganic elements in poultry manure during supercritical water gasification. 日本エネルギー学会誌 (J Jpn Inst Energ). 2008;87(9):731–6.
38. Demirbas A. Hydrogen-rich gas from fruit shells via supercritical water extraction. Int J Hydrogen Energ. 2004;29(12):1237–43.

39. Hao X, Guo L, Zhang X, Guan Y. Hydrogen production from catalytic gasification of cellulose in supercritical water. Chem Eng J. 2005;110(1–3):57–65.
40. Xu ZR, Zhu W, Htar SH. Partial oxidative gasification of municipal sludge in subcritical and supercritical water. Environ Technol. 2012;33(11):1217–23.
41. Yanik J, Ebale S, Kruse A, Saglam M, Yüksel M. Biomass gasification in supercritical water: II. Effect of catalyst. Int J Hydrogen Energ. 2008;33(17):4520–6.
42. Lu YJ, Guo LJ, Ji CM, Zhang XM, Hao XH, Yan QH. Hydrogen production by biomass gasification in supercritical water: a parametric study. Int J Hydrogen Energ. 2006;31(7): 822–31.
43. Kersten SR, Potic B, Prins W, Van Swaaij WP. Gasification of model compounds and wood in hot compressed water. Ind Eng Chem Res. 2006;45(12):4169–77.
44. Xu ZR, Zhu W, Li M. Influence of moisture content on the direct gasification of dewatered sludge via supercritical water. Int J Hydrogen Energ. 2012;37(8):6527–35.
45. Azadi P, Khan S, Strobel F, Azadi F, Farnood R. Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts. Appl Catal B Environ. 2012;117–118:330–8.
46. Madenoğlu TG, Kurt S, Sağlam M, Yüksel M, Gökkaya D, Ballice L. Hydrogen production from some agricultural residues by catalytic subcritical and supercritical water gasification. J Supercrit Fluid. 2012;67:22–8.
47. Kruse A, Maniam P, Spieler F. Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 2. Model compounds. Ind Eng Chem Res. 2007;46(1):87–96.
48. Stucki S, Vogel F, Ludwig C, Haiduc AG, Brandenberger M. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. Energy Environ Sci. 2009;2(5):535–41.
49. Sricharoenchaikul V. Assessment of black liquor gasification in supercritical water. Bioresour Technol. 2009;100(2):638–43.
50. Guan Q, Savage PE, Wei C. Gasification of alga *Nannochloropsis* in supercritical water. J Supercrit Fluid. 2012;61:139–45.
51. Yamamura T, Mori T, Park KC, Fujii Y, Tomiyasu H. Ruthenium (IV) dioxide-catalyzed reductive gasification of intractable biomass including cellulose, heterocyclic compounds, and sludge in supercritical water. J Supercrit Fluid. 2009;51(1):43–9.
52. Matsumura Y, Minowa T. Fundamental design of a continuous biomass gasification process using a supercritical water fluidized bed. Int J Hydrogen Energ. 2004;29(7):701–7.
53. Manarungson S, Mok WS, Antal MJ. Hydrogen production by gasification of glucose and wet biomass in supercritical water. In: Veziziroglu T, Takahashi PK, editors. Hydrogen energy progress VIII. Hawaii: Pergamon Press; 1990. p. 345–55.
54. Xu X, Antal MJ. Gasification of sewage sludge and other biomass for hydrogen production in supercritical water. Environ Prog. 1998;17(4):215–20.
55. Antal MJ, Allen SG, Schulman D, Xu XD, Divilio RJ. Biomass gasification in supercritical water. Ind Eng Chem Res. 2000;39(11):4040–53.
56. Matsumura Y. Evaluation of supercritical water gasification and biomethanation for wet biomass utilization in Japan. Energ Convers Manage. 2002;43(9–12):1301–10.
57. Matsumura Y, Harada M, Li D, Komiyama H, Yoshdda Y, Ishttani H. Biomass gasification in supercritical water with partial oxidation. Nihon Enerugi Gakkaishi (J Jpn Inst Energ). 2003;82(12):919–25.
58. Lu YJ, Ji CM, Guo LJ. Experimental investigation on hydrogen production by agricultural biomass gasification in supercritical water. J Xi'an Jiaotong Univ. 2005;39(3):239–42.
59. Lu YJ, Guo LJ, Hao XH, Ji CM. Influence of main parameters on wood sawdust gasification in supercritical water [J]. CIESC J. 2004;55(12):2060–6.
60. D'Jesús P, Boukis N, Kraushaar-Czarnetzki B, Dinjus E. Gasification of corn and clover grass in supercritical water. Fuel. 2006;85(7):1032–8.

61. Matsumura Y, Harada M, Nagata K, Kikuchi Y. Effect of heating rate of biomass feedstock on carbon gasification efficiency in supercritical water gasification. Chem Eng Commun. 2006;193(5):649–59.
62. Pei A, Zhang R, Jin H, Guo L. Research on catalysts and their catalytic characteristics for hydrogen production by gasification of peanut shell in supercritical water. J Xi'an Jiaotong Univ. 2008;7:027.
63. Chen J, Lu Y, Guo L, Zhang X, Xiao P. Hydrogen production by biomass gasification in supercritical water using concentrated solar energy: system development and proof of concept. Int J Hydrogen Energ. 2010;35(13):7134–41.
64. Byrd AJ, Kumar S, Kong L, Ramsurn H, Gupta RB. Hydrogen production from catalytic gasification of switchgrass biocrude in supercritical water. Int J Hydrogen Energ. 2011;36(5):3426–33.
65. Rönnlund I, Myréen L, Lundqvist K, Ahlbeck J, Westerlund T. Waste to energy by industrially integrated supercritical water gasification–Effects of alkali salts in residual by-products from the pulp and paper industry. Energy. 2011;36(4):2151–63.
66. Lu Y, Guo L, Zhang X, Ji C. Hydrogen production by supercritical water gasification of biomass: explore the way to maximum hydrogen yield and high carbon gasification efficiency. Int J Hydrogen Energ. 2011;37(4):3177–85.
67. Jarana G, Sánchez-Oneto J, Portela JR, Nebot Sanz E, Martínez de la Ossa EJ. Supercritical water gasification of industrial organic wastes. J Supercrit Fluid. 2008;46(3):329–34.
68. Hao XH, Guo LJ, Mao X, Zhang XM, Chen XJ. Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water. Int J Hydrogen Energ. 2003;28(1):55–64.
69. Lu YJ, Jin H, Guo LJ, Zhang XM, Cao CQ, Guo X. Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor. Int J Hydrogen Energ. 2008;33(21):6066–75.
70. Antal MJ. Hydrogen and food production from nuclear heat and municipal wastes. In: Veziroğlu TN, editor. Hydrogen energy. New York: Plenum Press; 1975. p. 331–8.
71. Kruse A, Henningsen T, Sinag A, Pfeiffer J. Biomass gasification in supercritical water; influence of the dry matter content and the formation of phenols. Ind Eng Chem Res. 2003;42(16):3711–7.
72. Chuntanapum A, Matsumura Y. Char formation mechanism in supercritical water gasification process: a study of model compounds. Ind Eng Chem Res. 2010;49(9):4055–62.
73. Antal MJ. The effects of reactor severity on the gas phase pyrolysis of cellulose and kraft lignin derived volatile matter. Ind Eng Chem Res. 1983;22:366–75.
74. Bühler W, Dinjus E, Ederer HJ, Kruse A, Mas C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near-and supercritical water. J Supercrit Fluid. 2002;22(1):37–53.
75. Sato T, Furusawa T, Ishiyama Y, Sugito H, Miura Y, Sato M, Suzuki N, Itoh N. Effect of water density on the gasification of lignin with magnesium oxide supported nickel catalysts in supercritical water. Ind Eng Chem Res. 2006;45(2):615–22.
76. Jin H, Lu Y, Guo L, Cao C, Zhang X. Hydrogen production by partial oxidative gasification of biomass and its model compounds in supercritical water. Int J Hydrogen Energ. 2010;35(7):3001–10.
77. Madenoğlu TG, Sağlam M, Yüksel M, Ballice L. Simultaneous effect of temperature and pressure on catalytic hydrothermal gasification of glucose. J Supercrit Fluid. 2012;73: 151–60.
78. Uematsu M, Frank EU. Static dielectric constant of water and steam. J Phys Chem Ref Data. 1980;9(4):1291–306.
79. Miller A, Hendry D, Wilkinson N, Venkitasamy C, Jacoby W. Exploration of the gasification of Spirulina algae in supercritical water. Bioresour Technol. 2012;119:41–7.
80. Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. Fuel Process Technol. 2001;73(3):155–73.

81. Elliott DC. Catalytic hydrothermal gasification of biomass. Biofuel Bioprod Biorefin. 2008;2(3):254–65.
82. Calzavara Y, Joussot-Dubien C, Boissonnet G, Sarrade S. Evaluation of biomass gasification in supercritical water process for hydrogen production. Energ Convers Manage. 2005;46(4):615–31.
83. Guo Y, Wang SZ, Xu DH, Gong YM, Ma HH, Tang XY. Review of catalytic supercritical water gasification for hydrogen production from biomass. Renew Sust Energ Rev. 2010;14(1):334–43.
84. Kruse A, Krupka A, Schwarzkopf V, Gamard C, Henningsen T. Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 1. Comparison of different feedstocks. Ind Eng Chem Res. 2005;44(9):3013–20.
85. Sinag A, Kruse A, Schwarzkopf V. Key compounds of the hydropyrolysis of glucose in supercritical water in the presence of K_2CO_3. Ind Eng Chem Res. 2003;42(15):3516–21.
86. Chakinala AG, Brilman DW, van Swaaij WP, Kersten SR. Catalytic and non-catalytic supercritical water gasification of microalgae and glycerol. Ind Eng Chem Res. 2009;49(3): 1113–22.
87. Bringas JE. Handbook of comparative world steel standards. 3rd ed. West Conshohocken: ASTM International; 2004. p. 4. ISBN 0-8031-3362-6.
88. Resende FL, Savage PE. Expanded and updated results for supercritical water gasification of cellulose and lignin in metal-free reactors. Energ Fuel. 2009;23(12):6213–21.
89. Boukis N, Diem V, Habicht W, Dinjus E. Methanol reforming in supercritical water. Ind Eng Chem Res. 2003;42(4):728–35.
90. Yu D, Aihara M, Antal Jr MJ. Hydrogen production by steam reforming glucose in supercritical water. Energ Fuel. 1993;7(5):574–7.
91. Manzour PA. Hydrogen production using catalytic supercritical water gasification of lignocellulosic biomass. PhD thesis, University of Toronto; 2012.
92. Boukis N, Galla U, D'Jesus P, Muller H, Dinjus E. Gasification of wet biomass in supercritical water: results of pilot plant experiments. In: 14th European biomass conference, 17–21 Oct, Paris, France; 2005. pp. 964–7.
93. Boukis N, Galla U, Müller H, Dinjus E. Biomass gasification in supercritical water. Experimental progress achieved with the VERENA pilot plant. In: 15th European conference & exhibition, 7–11 May, Berlin, Germany 7; 2007. pp. 1013–6
94. Kruse A. Supercritical water gasification. Biofuel Bioprod Biorefin. 2008;2(5):415–37.
95. Matsumura Y, Minowa T, Potic B, Kersten SRA, Prins W, van Swaaij WPM, van de Beld B, Elliott DC, Neuenschwander GG, Kruse A, Antal MJ. Biomass gasification in near- and super-critical water: status and prospects. Biomass Bioenerg. 2005;29(4):269–92.
96. Hodes M, Marrone PA, Hong GT, Smith KA, Tester JW. Salt precipitation and scale control in supercritical water oxidation—Part A: fundamentals and research. J Supercrit Fluid. 2004;29(3):265–88.
97. Marrone PA, Hodes M, Smith KA, Tester JW. Salt precipitation and scale control in supercritical water oxidation—Part B: commercial/full-scale applications. J Supercrit Fluid. 2004;29(3):289–312.
98. Loppinet-Serani A, Aymonier C, Cansell F. Current and foreseeable applications of supercritical water for energy and the environment. ChemSusChem. 2008;1(6):486–503.
99. Peterson AA, Vogel F, Lachance RP, Fröling M, Antal Jr MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: a review of sub-and supercritical water technologies. Energ Environ Sci. 2008;1(1):32–65.
100. Waldner MH, Vogel F. Renewable production of methane from woody biomass by catalytic hydrothermal gasification. Ind Eng Chem Res. 2005;44(13):4543–51.